



Development of a catalytic ceramic foam for efficient tar reforming of a catalytic filter for hot gas cleaning of biomass-derived syngas

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ARTICLE INFO

Article history:

Received 7 December 2011

Received in revised form 15 May 2012

Accepted 18 May 2012

Available online 1 June 2012

Keywords:

Catalytic ceramic foam

Catalytic filter

NiO

Tar reforming

Biomass gasification

Hot gas cleaning

ABSTRACT

In order to improve the tar reforming performance of a catalytic filter in hot gas cleaning of biomass-derived syngas, as new approach, 45 ppi ceramic foams of 10 mm wall thickness were used as ceramic support for catalyst integration. Screening of this ceramic support was performed by varying the type of catalyst support, its loading and the NiO loading. As a result, a SiC ceramic foam with a MgO–Al₂O₃–NiO catalytic layer, a catalyst support density of 0.03 g/cm³ and a NiO density of 0.02 g/cm³ was identified as most active catalytic ceramic foam. After the transfer of the corresponding impregnation procedure to an Al₂O₃ based ceramic foam to be able to operate at the target filtration temperature of 850 °C, a naphthalene conversion of 99% was achieved at a superficial velocity of 2.5 cm/s in the presence of 100 ppmv H₂S. At doubled superficial velocity the conversion still achieves 93%. The transfer of the catalyst integration procedure for the most active SiC candle supported MgO–Al₂O₃–NiO layer to an Al₂O₃ filter candle with 10 mm wall thickness has led to a naphthalene conversion of 87% at 850 °C at a superficial velocity of 2 cm/s in the presence of 100 ppmv H₂S being 8% higher than in the SiC based candle. The combined Al₂O₃ based catalytic filter and ceramic foam disk system shows an overall conversion of 99% at a superficial velocity of 2 cm/s. Based on these results the corresponding overall conversion of an Al₂O₃ based catalytic filter candle with integrated catalytic ceramic foam was precalculated to 98% at 850 °C in the presence of 100 ppmv H₂S indicating the technical feasibility of efficient tar reforming using this novel catalytic filter candle design.

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1. Introduction

The increasing scarceness of fossil fuels and more stringent regulations with regard to CO₂ emissions are the reasons why gasification of sustainably produced biomass, regarded as a roughly CO₂ neutral feedstock after transportation, distribution and combustion [1,2], is of increasing interest in the energy and fuel production sector. The main problem in gasification of biomass that has to be overcome is tar removal. As prerequisite to solve the tar problem, an advanced gasification technology generating low tar contents between 2 [3] and 4 g/Nm³ [4] in the raw syngas is to be applied. This can be realized on commercial scale e.g. by a dual fluidized bed gasification process using olivine as reactive bed material [5] and operating the gasifier in the middle-temperature range of about 850 °C to allow an energy-efficient syngas production. The corresponding raw gas temperature of ≥800 °C allows tar removal by catalytic tar reforming using Ni based catalysts [6,7]. Catalytic tar reforming can be cost-effectively combined with hot gas filtration

for fine particle separation, if using a catalytic filter [8,9]. Two different designs of a catalytic tar reforming hot gas filter were presented in previous work [10–13]. In the first presented catalytic filter of fixed bed design, that has been proven to be the most active catalytic filter under model gas [13] and real gas conditions [14,15], the catalyst was integrated as fixed bed into the hollow-cylindrical space of a tube in candle design. In the second presented catalytic filter of catalytic layer design the catalyst was integrated on the pore walls of the filter candle [11]. This candle has only shown an activity of 73% conversion at a filtration velocity of 2.5 cm/s at 800 °C in the presence of 100 ppmv H₂S at a naphthalene inlet content of 5 g/Nm³ compared to complete conversion of the first presented catalytic filter candle [13]. Nevertheless, this catalytic activity was very promising as being evidently dependent on the relatively high pore volume of 50 vol% for a grain-sintered filter element support. In a comparison of different catalytic layers on a grain-sintered filter element support with a lower pore volume of only 38 vol%, the catalytic activity could not be increased above a value of 58% conversion under comparable conditions [11,13]. Consequently, higher catalytic activities with the catalytic layer design should be achieved, if a modified or new filter element support with a higher pore volume is used.

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From the manufacturing point of view, catalytic filter elements of catalytic layer design allow a distinct simplification of the manufacturing procedure leading to distinctly lower manufacturing costs than in case of the fixed bed design. Therefore, in this work a new approach is followed by presenting catalytically activated 45 ppi ceramic foams as additional reforming step for integration into the hollow-cylindrical space of a catalytic filter element without causing an additional differential pressure at a superficial velocity between 4 and 5 cm/s (Fig. 1).

In the first part of this article the development of the most active catalytic layer on a SiC based ceramic foam disk is described in an activity screening study at different temperatures and superficial velocities in the presence and absence of H₂S using naphthalene as tar model compound in model biomass gasification gas.

With regard to started activities to integrate such a catalytic filter element directly inside the gasifier freeboard for further cost reduction [16], Al₂O₃ is to be selected as filter material because of the high gasifier freeboard temperatures of >800 °C up to 850 °C. Therefore, in the second part of this article the most active catalytic layer system on a SiC based ceramic foam and the most active catalytic layer system on a SiC filter element identified in previous work [11] were transferred to appropriately manufactured Al₂O₃ based ceramic foam and filter element supports that can withstand the higher operating temperature in the gasifier freeboard.

Finally, a combination of an Al₂O₃ based catalytic filter element as first reforming step and Al₂O₃ based ceramic foam as second reforming step is examined on its catalytic activity at different superficial velocities to be able to calculate the overall catalytic activity of the novel catalytic filter element sketched in Fig. 1.

2. Experimental

2.1. Manufacturing of SiC and Al₂O₃ based ceramic foams

SiC and Al₂O₃ based ceramic foams of 45 ppi (pores per inch), respectively, were manufactured according to the replica method [17,18]. Polyurethane foams of appropriate outer diameter and thickness to adjust the final outer diameter of 28 mm and 10 mm thickness were coated with a SiC and Al₂O₃ based ceramic slurry. The coated substrates were then squeezed out by using a rolling machine followed by drying at room temperature and subsequent sintering.

2.2. Catalyst integration

2.2.1. Preparation of a SiC and Al₂O₃ based catalytic filter candle

The preparation of a catalytic grain-sintered (GS) SiC based filter candle segment of 60 mm outer diameter, 40 mm inner diameter and 50 mm length with a pore volume of 38 vol% according to the incipient wetness technique was already described in previous work [11,13]. The same procedure was applied here by using a grain-sintered Al₂O₃ based candle with a pore volume of 45 vol%.

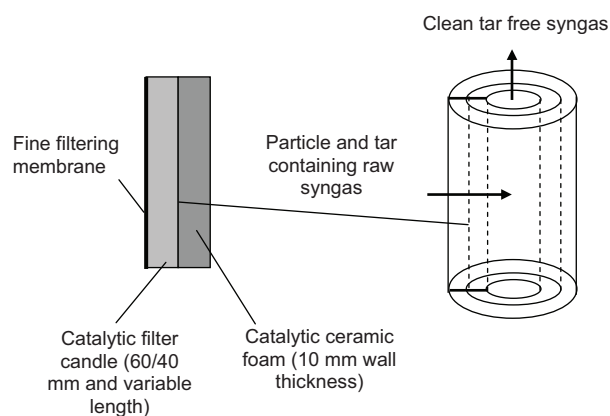


Fig. 1. Structure of the catalytic filter candle with integrated catalytic ceramic foam.

In Table 1 the corresponding composition of the catalytic layers are presented. The corresponding loading amounts of the catalyst support adjusted after impregnation with the appropriate MgO–Al₂O₃ precursor suspension, ZrO₂–MgO–Al₂O₃ precursor suspension or magnesium nitrate hexahydrate solution, respectively, are given as weight percentages related to the mass of the ceramic support in the sample notation.

To adjust the high MgO–Al₂O₃ loading amount in sample CFO–SiC–5.5MgAl–68Ni (CFO = ceramic foam), a two-fold impregnation was applied.

In addition, in the sample notations, the corresponding NiO loadings are given as weight percentages related to the mass of the catalyst support after using 13.5% nickel nitrate hexahydrate solutions in the catalytic impregnation process for the samples. In deviation from the standard preparation procedure, for the samples CFO–SiC–5.5MgAl–68Ni and CFO–Al–6.2MgAl–59Ni a 18.9% nickel nitrate hexahydrate solution and for the sample CFO–SiC–1.9ZrMgAl–322Ni a 24% nickel nitrate hexahydrate solution were used.

For comparison purposes, the catalyst support and NiO densities of the catalytic filter samples are also given in Table 1.

2.2.2. Preparation of catalytic SiC and Al₂O₃ based ceramic foams and a SiO₂–Al₂O₃ based ceramic fiber

Catalytic ceramic foam disks and a catalytic SiO₂–Al₂O₃ (SiAl) based ceramic fiber (CFI) disk of 28 mm outer diameter and 10 mm thickness were prepared by applying the wet impregnation method. In a first step, the ceramic foams were dipped into the appropriate catalyst support precursor suspension or solution, respectively, followed by infrared drying of the sample and sintering. In a second step, the coated ceramic foam or ceramic fiber, respectively, were dipped in an appropriately concentrated nickel nitrate hexahydrate solution (see Table 1). After complete infrared drying, the samples were sintered at 900 °C. The compositions of the appropriate catalytic layers are given in Table 1. In the notation

Table 1
Characterization of catalytic layers of SiC and Al₂O₃ based grain-sintered filter elements, ceramic foams and an Al₂O₃–SiO₂ based ceramic fiber.

Sample notation	Catalyst support	Catalyst support density (g/cm ³)	Catalyst support density normalized (g/cm ³)	NiO density (g/cm ³)	NiO density normalized (g/cm ³)
GS–SiC–0.8MgAl–60Ni	MgO–Al ₂ O ₃	0.0156	1.00	0.0093	1.00
GS–Al–0.7MgAl–77Ni	MgO–Al ₂ O ₃	0.0157	–	0.0120	–
CFO–SiC–2.4MgAl–125Ni	MgO–Al ₂ O ₃	0.0148	0.95	0.0185	1.99
CFO–SiC–5.5MgAl–68Ni	MgO–Al ₂ O ₃	0.0295	1.89	0.0200	2.15
CFO–SiC–1.9ZrMgAl–322Ni	ZrO ₂ –MgO–Al ₂ O ₃	0.0106	–	0.0340	–
CFO–SiC–4.1ZrMgAl–84Ni	ZrO ₂ –MgO–Al ₂ O ₃	0.0247	–	0.0207	–
CFO–SiC–4Mg–99Ni	MgO	0.0202	–	0.0200	–
CFI–SiAl–21MgAl–62Ni	MgO–Al ₂ O ₃	0.0494	3.17	0.0307	3.30
CFO–Al–6.2MgAl–59Ni	MgO–Al ₂ O ₃	0.0364	–	0.0215	–

Table 2

Pore volume of different types of porous ceramic supports.

Sample notation	Type of ceramic support	Pore volume (vol%)
GS-SiC	Grain-sintered filter element	38
CFO-SiC	Ceramic foam (45 ppi)	71
CFI-SiAl	Ceramic fiber	98

of the samples the weight percentages of the catalyst support and NiO are indicated. In addition, the corresponding catalyst support and NiO densities are given.

2.3. Characterization

2.3.1. Determination of pore volume

The pore volume of the prepared SiC based ceramic filter element segments, 45 ppi ceramic foams and the SiO₂–Al₂O₃ based ceramic fiber was determined by pore filling with water. Three candle segments of the dimension 60/40 mm × 50 mm as well as ceramic foam and ceramic fiber disk samples, respectively, with the dimension of 28 mm outer diameter and 10 mm thickness were filled with water. Evacuation of the samples was performed in case of the filter element samples before water filling. The appropriate pore volumes of the examined samples calculated from the loading amount of water are given in Table 2.

2.3.2. Determination of the specific (BET) surface area

The specific surfaces of the catalytic filter element, ceramic foam and ceramic fiber samples according to the BET (Brunauer–Emmett–Teller) method were measured by using Krypton as test gas and a Quantachrome AUTOSORB-3. Appropriate samples of the grain-sintered filter element were prepared by cutting out 12 pieces from an 8 mm thick hollow-cylindrical filter element segment. Ceramic foam based samples were prepared by crushing the appropriate disk and sieving out a particle fraction with particle sizes between 1 and 3 mm. A fraction of comparable particle sizes was cut out from the ceramic fiber based sample. The corresponding BET values of the different catalytically activated samples are given in Table 3. In addition to the specific surface area of the catalytically activated samples, the calculated surface area per sample volume in m²/cm³ are given in Table 3.

2.4. Measurement of the catalytic activity

The catalytic activity of ceramic foam and filter element samples in reforming of naphthalene as tar model compound was measured under comparable conditions as described in detail in previous work [10].

For activity measurements of catalytic ceramic foams and a ceramic fiber disk, samples of 28 mm outer diameter and 10 mm

thickness were prepared and integrated into an Al₂O₃ tube reactor. For activity measurements of catalytic filter element samples, disk-like samples of 28 mm outer diameter and 10 mm thickness were drilled out from catalytic filter candles of 60 mm outer diameter and 40 mm inner diameter.

For the measurement of the combined system, in a first step the catalytic candle segment was inserted into the middle of a 500 mm long Al₂O₃ tube. In a second step, the catalytic ceramic foam segment was integrated with a distance of 24 mm from the candle segment.

Model biomass gasification gas of the composition 50% N₂, 12% CO, 10% H₂, 11% CO₂, 5% CH₄ and 12% H₂O with a naphthalene content of 5 g/Nm³ was used to simulate raw syngas from gasifiers that are operated with an air-steam mixture. An examination of a catalytic filter candle of same composition under a model gas composition, where a higher water content of up to 30 vol% was used, has shown comparable naphthalene conversions [12] compared to the above selected model gas. Thus, gained naphthalene conversions under the model gas conditions in this work should also have validity for raw syngases from steam-blown gasifiers. For H₂S deactivation studies, a content of 100 ppmv H₂S was adjusted in the model biomass gasification gas.

In all activity measurements the samples were activated in situ by reducing the containing NiO to the catalytically active Ni metal at 900 °C for 30 min in model biomass gasification gas without naphthalene before the start of the activity measurement campaign.

The naphthalene conversion at each temperature point was measured as an average value of 960 measurement points over a time interval of 1 h by means of an online quadrupole mass spectrometer MS Balzers QMA 200 that allows also the determination of the relative content of the main gas components N₂, H₂, CO, CO₂ and CH₄. A corresponding measurement error of ±1% (absolute percentage) is to be taken into account in the naphthalene conversion measurements.

2.5. SEM/EDX (energy dispersive X-ray) microscopy

SEM/EDX was used to determine the NiO crystallite size. The analysis was performed on a LEO (Leitz Elektronen Optik) 1455 VP with an acceleration voltage of 20 kV and operating with a wolfram cathode. The corresponding K_α line was used to identify NiO.

Appropriate samples were prepared by cutting out a piece of the dimension 8 × 5 × 10 mm from the 10 mm thick catalytic ceramic foam disks followed by sputtering with gold.

3. Results and discussion

3.1. Activity comparison of catalytic porous ceramics of different porosity

For the right selection of a highly porous ceramic that can be integrated into the hollow-cylindrical space of a grain-sintered

Table 3

Specific (BET) surface, corresponding surface area per sample volume of catalytically activated SiC/Al₂O₃ based grain-sintered filter elements, ceramic foams and an Al₂O₃–SiO₂ based ceramic fiber as well as NiO crystallite size determined by SEM/EDX of the samples CFO-SiC-5.5MgAl-68Ni and CFO-SiC-4Mg-99Ni.

Sample notation	Specific surface area (BET) (m ² /g)	Surface area/sample volume (m ² /cm ³)	NiO crystallite size (nm)
GS-SiC-0.8MgAl-60Ni	0.91	1.74	–
GS-Al-0.7MgAl-77Ni	0.57	1.24	–
CFO-SiC-2.4MgAl-125Ni	1.6	1.00	–
CFO-SiC-5.5MgAl-68Ni	4.6	2.70	30 ± 5
CFO-SiC-1.9ZrMgAl-322Ni	1.5	0.90	–
CFO-SiC-4.1ZrMgAl-84Ni	1.87	1.21	–
CFO-SiC-4.0Mg-99Ni	1.8	0.99	45 ± 5
CFI-SiAl-21MgAl-62Ni	18.3	5.57	–
CFO-Al-6.2MgAl-59Ni	5.1	3.28	–

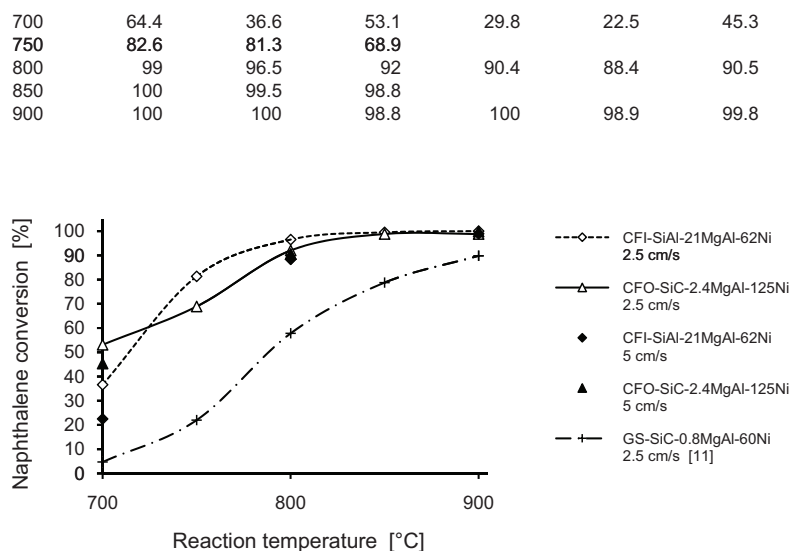


Fig. 2. Naphthalene conversion in the presence of 100 ppmv H_2S versus reaction temperature of catalytic layers on different ceramic supports after using the same impregnation media.

catalytic filter element and does not cause an additional differential pressure at typical filtration velocities between 4 and 5 cm/s, a 45 ppi SiC based ceramic foam (sample CFO-SiC) and a $SiO_2-Al_2O_3$ based ceramic fiber (sample CFI-SiAl) were impregnated with catalyst. The same catalyst support precursor suspension and nickel nitrate solution as applied for the grain-sintered catalytic filter element (sample GS-SiC-0.8MgAl-59Ni) developed in previous work [11] was applied. The realized catalyst loadings after applying a wet impregnation procedure are given in Table 1. The corresponding catalyst support and NiO densities and the corresponding normalized values in relation to the appropriate values of the catalytic filter element GS-SiC-0.8MgAl-59Ni are also given in Table 1. The appropriate specific surface and surface in m^2/cm^3 are given in Table 3.

The catalytic activity of the three samples in the presence of 100 ppmv H_2S using model biomass gasification and naphthalene as tar model compound at a superficial velocity of 2.5 and 5 cm/s is displayed in Fig. 2. The higher superficial velocity was chosen to simulate the conditions when a porous ceramic is integrated into a cylindrical catalytic filter element of 60 mm outer diameter and 40 mm inner diameter according to the design in Fig. 1. Under these conditions an average superficial velocity of 4.67 cm/s would result for the porous ceramic hollow cylinder, if the catalytic filter is operated with a superficial velocity of 2 cm/s.

Fig. 2 shows clearly, that catalytic conversions above 90% are achieved at the lowest target temperature of 800 °C in the presence of 100 ppmv H_2S , if using an aluminum silicate based ceramic fiber or a 45 ppi SiC based ceramic foam instead of a grain-sintered SiC ceramic for catalyst integration. The latter shows only a conversion of 58% [11]. The higher activities of the ceramic fiber and the 45 ppi based ceramic foam are directly due to the distinctly higher NiO densities that result from the higher pore volume of 98 and 71 vol% in both samples after applying the wet impregnation procedure (see Table 1 and 2). Evidently, doubling the NiO density in the ceramic foam sample by keeping the catalyst support loading constant compared to the catalytic filter element sample is most effective, because a tripling of the NiO and catalyst support density in case of the ceramic fiber sample does not lead to a distinctly higher activity. If the superficial velocity is increased from 2.5 to 5 cm/s, the catalytic activity of the 45 ppi catalytically activated ceramic foam is with 91% naphthalene conversion even higher than in case of the catalytic ceramic fiber, that shows only

88% conversion. The 5.6-fold higher sample surface of the catalytic ceramic fiber of $5.6 m^2/cm^3$ compared to the ceramic foam, evidently, has no positive effect on the activity (Table 3). Possibly, flow conditions are distinctly changed in case of a catalytic ceramic fiber in blocking the open pathways by the high catalyst loading amount of 21 wt% $MgO-Al_2O_3$ and 13 wt% NiO that present rather a catalyst filling than a catalytic coating. This assumption was verified by detailed SEM examinations that cannot be presented within the frame of this work. In case of the catalytic ceramic foam the sample surface is with $1 m^2/cm^3$ even by 1.74 lower than in the catalytic grain-sintered filter element (see Table 3). Referring to the lower total catalyst loading of 5.4 wt% of the catalytic ceramic foam, the achieved catalytic activity of this sample indicates better flow-through conditions and a better exploitation of the integrated catalyst amount compared to the total catalyst loading of 34 wt% of the catalytic ceramic fiber (see Table 1).

Moreover, compared to a catalyst filled ceramic fiber a catalytically activated ceramic foam provides a higher mechanical stability because of its rigidity. Therefore, not only because of the slightly higher activity at a superficial velocity of 5 cm/s, but especially with respect to its easier handling during the integration procedure into a catalytic filter candle, the 45 ppi ceramic foam presents the most suitable solution to improve the overall catalytic activity of a catalytic filter candle of the design sketched in Fig. 1.

3.2. Screening of activity of different ceramic foam supported catalytic layers

For the determination of the most active catalytic layer on a SiC based ceramic foam, an activity screening of five different catalytic layers was performed by varying the type of the catalyst support material, its loading amount and the NiO loading (see Table 1).

In a previous work [10] it was shown that the use of a basic catalyst support material like MgO is very promising for the naphthalene reforming reaction and can prevent the adsorption of polyaromatic intermediates as precursors of carbon deposits in case of incomplete reforming of a supported Ni catalyst [19]. Therefore, MgO was also used in this work and presents the only or main component in the mixed oxides, respectively, in the five different catalytic layers on SiC ceramic foams. To prepare catalyst support materials with a high BET surface, mixed oxide materials with 70% MgO and 30% Al_2O_3 or 68% MgO, 10% ZrO_2 and 22%

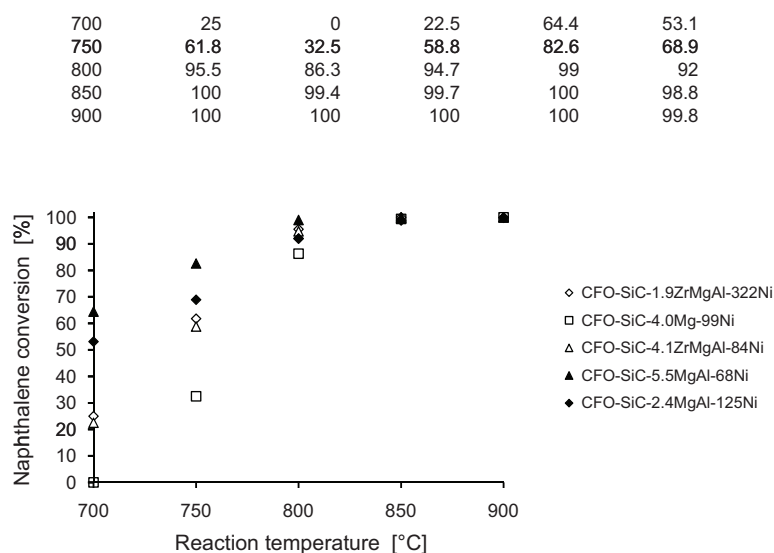


Fig. 3. Naphthalene conversion in the presence of 100 ppmv H_2S versus reaction temperature of different catalytic layers on SiC based ceramic foams at a superficial velocity of 2.5 cm/s.

Al_2O_3 , respectively, have been found suitable in the preparation of catalytic layers on SiC based ceramic filter elements [11,13]. It is expected from the comparison of the surface charge properties of ZrO_2 with Al_2O_3 [20], that the content of ZrO_2 in the $\text{MgO-ZrO}_2\text{-Al}_2\text{O}_3$ does not cause a distinct change compared to the basicity of the mixed $\text{MgO-Al}_2\text{O}_3$ support.

By this reason, two of five catalytic layers consists of a $\text{MgO-Al}_2\text{O}_3$ support and further two consists of a $\text{MgO-ZrO}_2\text{-Al}_2\text{O}_3$ support with an appropriately different catalyst support and NiO loading.

Figs. 3 and 4 show the corresponding naphthalene conversion in the presence of H_2S at the superficial velocities 2.5 and 5 cm/s, respectively.

Fig. 3 shows, that at 800 °C and a superficial velocity of 2.5 cm/s in the presence of 100 ppmv H_2S complete naphthalene conversion is achieved with the sample CFO-SiC-5.5MgAl-68Ni, which is only decreasing to 90%, if the superficial velocity is doubled (see Fig. 4). This is the highest naphthalene reforming activity achieved in the presence of 100 ppmv H_2S using any catalytically activated porous ceramic so far [11,13]. The high activity is caused by the

integration of a high catalyst support amount and a sufficiently high NiO loading.

The following sequence of activity can be ruled out from Fig. 3 at the temperature point 750 °C where increased H_2S blocking occurs and small differences in the activity of the catalytic layer systems are better visible:

$$\begin{aligned} &\text{CFO-SiC-5.5MgAl-68Ni} > \text{CFO-SiC-2.4MgAl-125Ni} \\ &> \text{CFO-SiC-1.9ZrMgAl-322Ni} > \text{CFO-SiC-4.1ZrMgAl-84Ni} \\ &> \text{CFO-SiC-4Mg-99Ni} \end{aligned}$$

This order of activity can be explained, if the NiO density, catalyst support density (see Table 1) and BET surface area per sample volume (see Table 3) are compared. For a better overview, the normalized values in relation to the sample CFO-SiC-2.4MgAl-125Ni as reference sample are displayed in Fig. 5.

The appropriate data of the most active sample CFO-SiC-5.5MgAl-68Ni compared to the value of the sample of second high activity CFO-SiC-2.4MgAl-125Ni reveal that the increase in the

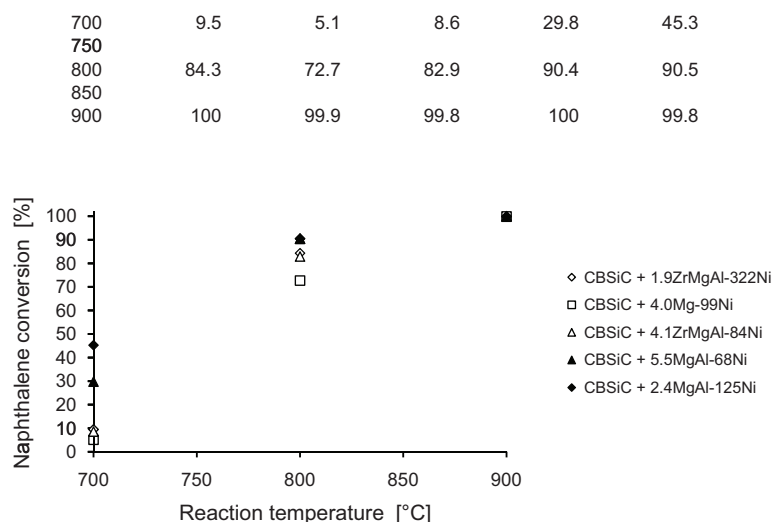


Fig. 4. Naphthalene conversion in the presence of 100 ppmv H_2S versus reaction temperature of different catalytic layers on SiC based ceramic foams at a superficial velocity of 5 cm/s.

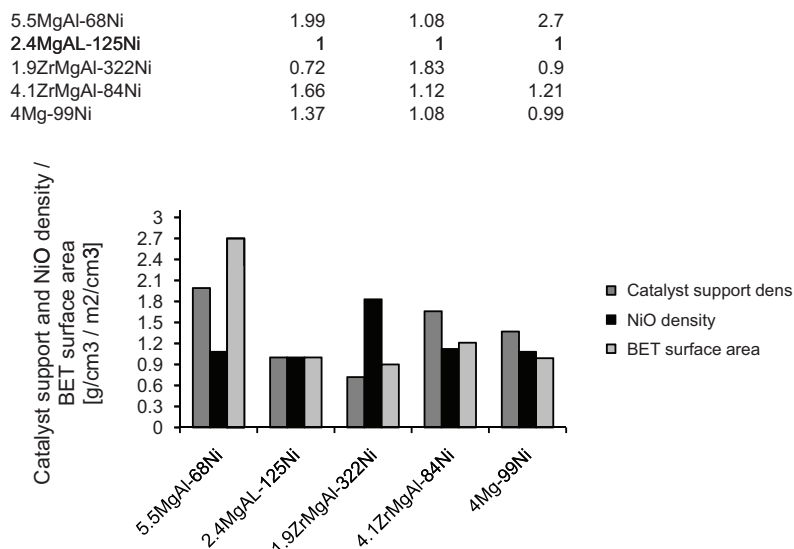


Fig. 5. Catalyst support density, NiO density and BET surface area of five SiC ceramic foam supported catalytic layer systems with decreasing catalytic activity.

catalyst support loading by a factor of 2.29 combined with a 25% increase in the NiO loading resulted in a BET surface increase by a factor of 3. Consequently, the best catalytic performance was observed. After substitution of the catalyst support material MgO-Al₂O₃ of sample CFO-SiC-2.4MgAl-125Ni by ZrO₂-MgO-Al₂O₃ and increase in the catalyst support density by a factor of 1.7 at a 12% higher NiO density, a BET surface increase of 21% is realized (see sample SiC-4.1ZrMgAl-84Ni). If the catalyst support material MgO-Al₂O₃ of sample CFO-SiC-2.4MgAl-125Ni is substituted by MgO and the catalyst support density is increased by a factor of 1.4 at a 8% higher NiO density, no change of the BET surface results (see sample CFO-SiC-4Mg-99Ni). The resulting lower activity of both samples being even lower in the latter sample can be explained by the type of the catalyst support material. Evidently, a ZrO₂ doped MgO-Al₂O₃ and a MgO based support seem to be a less suitable support compared to MgO-Al₂O₃. Possibly, the extent of forming solid solutions with NiO could be different in the ZrO₂ doped MgO-Al₂O₃ and MgO support compared to the MgO-Al₂O₃ support leading to different reducibilities and resulting activities of the supported Ni catalysts. Within the frame of this screening work the contribution of the catalyst support type on the catalytic activity could not be examined in more detail due to the limited number of prepared samples and the lack of samples with exactly the same NiO loading compared to the reference sample.

It is remarkable, that in consistency to previous work [11] also in this work it can be shown, that the relatively high NiO density in sample CFO-SiC-1.9ZrMgAl-322Ni leads to the third highest catalytic activity, even if the BET surface is slightly lowered by a relatively low catalyst support loading.

To reveal a potential relationship between the catalytic activity and the NiO particle size the most active catalytic layer system CFO-SiC-5.5MgAl-68Ni based on the MgO-Al₂O₃ support and the less active catalytic layer system based on the MgO support were examined on the NiO particle size by means of SEM/EDX. For the most active catalytic layer system a NiO particle size of 30 ± 5 nm was found, whereas for the less active catalytic layer system CFO-SiC-4Mg-99Ni a NiO particle size of 45 ± 5 nm was measured (see Table 3). Evidently, the higher catalytic activity in the MgO-Al₂O₃ supported Ni catalyst can also be related to a smaller NiO particle size compared to the MgO supported Ni catalyst. As a particle size of 25 nm is the resolution limit of the applied SEM microscope, more detailed SEM examinations coupled with an examination of

the catalyst support interactions of different catalyst supports of comparable NiO loadings could be objective of a subsequent future work by using a field emission gun SEM microscope with a distinctly higher resolution.

3.3. Catalytic activity of an Al₂O₃ based catalytic filter candle and ceramic foam

To provide a catalytic filter solution for the higher gasifier free-board temperature of about 850 °C, where SiC cannot be applied, because it would suffer a chemical attack under these operating conditions, an Al₂O₃ based filter and ceramic foam were developed. For the integration of catalyst in these new porous ceramics, the same impregnation procedures were applied as used to prepare the most active catalytic layer on a grain-sintered SiC filter element (GS-SiC-0.8MgAl-59Ni) and a SiC based ceramic foam (CFO-SiC-5.5MgAl-68Ni).

The as-prepared Al₂O₃ based catalytic filter candle GS-Al-0.7MgAl-77Ni shows a similar catalyst support and a higher NiO loading compared to the appropriate SiC support, whereas a lower BET surface of 1.24 m²/cm³ is achieved compared to 1.74 m²/cm³ of the SiC based sample (see Tables 1 and 3).

In case of the Al₂O₃ based ceramic foam CFO-Al-6.2MgAl-59Ni a higher BET surface of 3.28 m²/cm³ was achieved compared to the value of 2.7 m²/cm³ of the SiC based ceramic foam that is in line with the higher NiO and catalyst support densities (see Tables 1 and 3).

The appropriate naphthalene conversion of the catalyst containing Al₂O₃ based catalytic filter element in the presence and absence of H₂S at the temperature points 800, 850 and 900 °C as well as at a target superficial velocity of 2 cm/s are displayed in Figs. 6 and 7. The corresponding conversions of the catalyst containing Al₂O₃ based ceramic foam at a superficial velocity of 2.5 cm/s are also given in these figures.

A comparison of the appropriate activity of sample GS-Al-0.7MgAl-77Ni at 800 and 850 °C in the presence of H₂S (Fig. 6) with the activity of sample GS-SiC-0.8MgAl-59Ni (Fig. 2) shows for the Al₂O₃ based sample at both temperatures at a superficial velocity of 2 cm/s by 8 or 10 absolute percentage higher activity values, respectively, that can be explained with the higher NiO density of 0.012 g/cm³ compared to 0.0093 g/cm³ in the SiC based filter

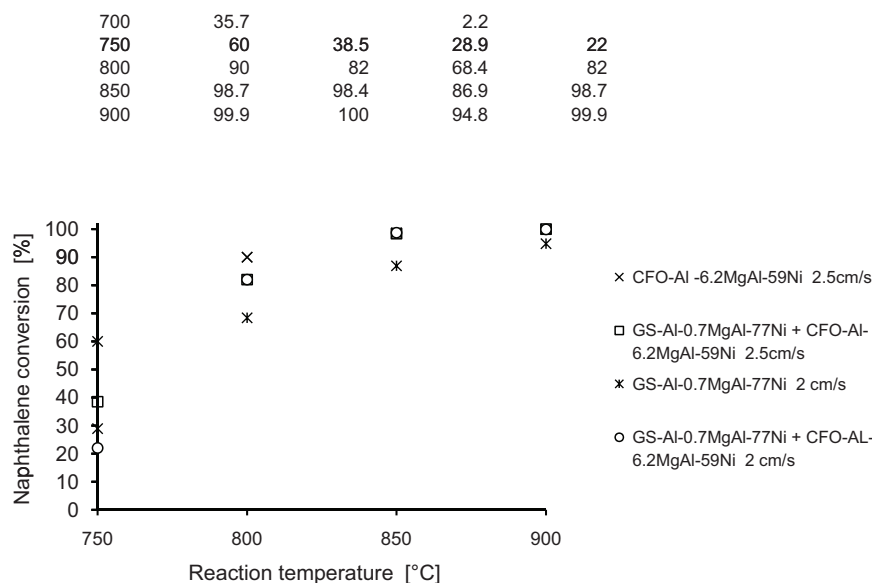


Fig. 6. Naphthalene conversion versus reaction temperature in the presence of 100 ppmv H_2S of the Al_2O_3 candle and ceramic foam supported catalytic layer systems in separate and combined mode at different superficial velocities.

sample. At 800 and 850 °C naphthalene conversions of about 68 and 87%, respectively, are achieved.

In the absence of the catalyst poison H_2S the catalytic activity increases up to 92% at 800 °C, because H_2S blocking of Ni active sites is suspended (Fig. 7).

An activity comparison of the Al_2O_3 based ceramic foam CFO-Al-6.2MgAl-59Ni (Fig. 6) with the SiC based ceramic foam CFO-SiC-5.5MgAl-68Ni (Fig. 3) shows at 800 and 850 °C in the presence of H_2S at a superficial velocity of 2.5 cm/s that the naphthalene conversion are 90 and 99%, whereas the SiC based catalytic ceramic foam shows nearly complete conversion at both temperatures.

At a superficial velocity of 5 cm/s, the Al_2O_3 based catalytic ceramic foam still shows a high naphthalene conversion of 93% at 850 °C (not shown in Fig. 6).

In the absence of H_2S , the Al_2O_3 based catalytic ceramic foam shows at 800 °C a conversion of 97% at a face velocity of 2.5 cm/s (Fig. 7). This indicates that naphthalene is not completely reformed at 800 °C to be further investigated in detail in future work, because

if a SiC based ceramic foam is used, complete naphthalene conversion was found under same conditions (not shown in Fig. 3).

The results in the presence and absence of H_2S show, that a temperature of 850 °C would be more convenient to an Al_2O_3 based catalytic ceramic foam at this development status. The target gasifier freeboard temperature would fit to this type of ceramic foam.

Figs. 6 and 7 display also the activity in the presence and absence of H_2S in an arrangement of an Al_2O_3 based catalytic filter element as first reforming step combined with an Al_2O_3 based ceramic foam as second reforming step in flow direction at a superficial velocity of 2 and 2.5 cm/s. This activity examination is an approximation to the conditions of a cylindrical catalytic filter element with integrated catalytic ceramic foam as sketched in Fig. 1.

Fig. 6 shows, that the catalytic activity of a combination of an Al_2O_3 based catalytic filter element and catalytic ceramic foam in the presence of 100 ppmv H_2S is distinctly increased compared to the Al_2O_3 based catalytic filter element alone. At 800 °C an increase from 68.4 to 82% and, at the target temperature of 850 °C, an

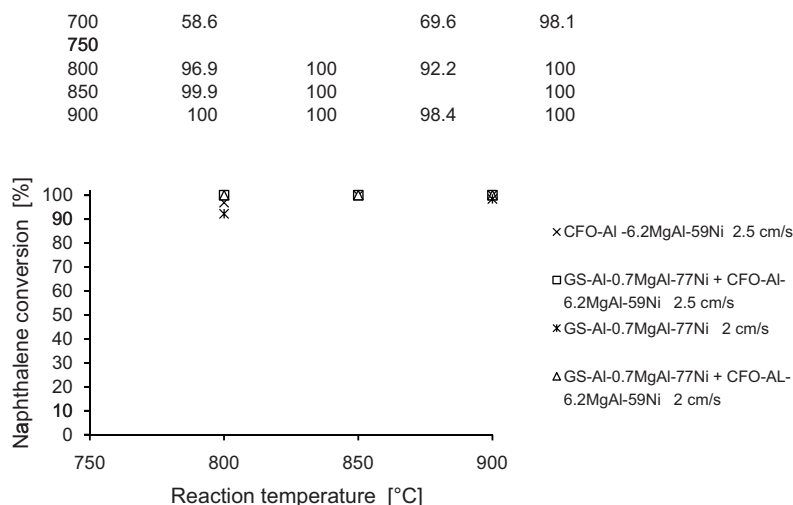


Fig. 7. Naphthalene conversion versus reaction temperature in the absence of H_2S of the Al_2O_3 candle and ceramic foam supported catalytic layer systems in separate and combined mode at different superficial velocities.

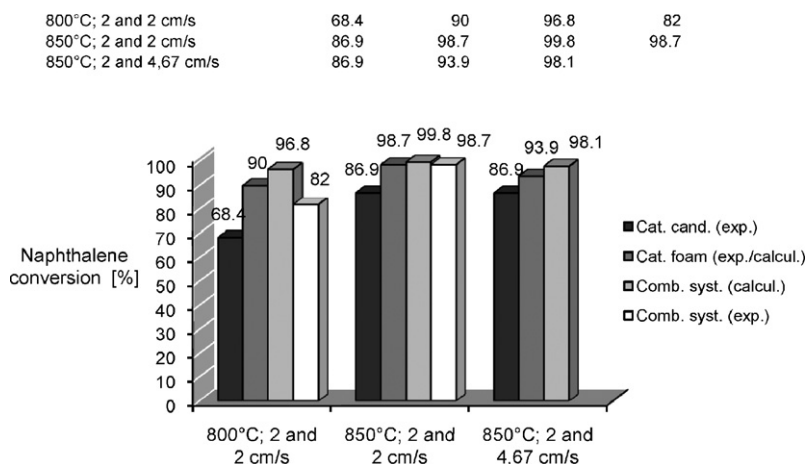


Fig. 8. Measured or calculated conversion in the presence of 100 ppmv H_2S for the separate catalytic systems GS-Al-0.7MgAl-77Ni and CFO-Al-6.2MgAl-59Ni or the combined system, respectively, at different operating temperatures and superficial velocity combinations.

increase from 86.9 to 98.7% is achieved, if in addition to the catalytic filter element the catalytic ceramic foam is used for naphthalene reforming at a superficial velocity of 2 cm/s. An examination of the corresponding methane conversions has shown, that also the methane conversions increase from 4.8 to 11.6% at 800 °C and from 14.2 to 36.4% at 850 °C (not shown in Fig. 6). These results confirm the distinct increase of the catalytic activity, if the catalytic filter element is combined with a catalytic ceramic foam as second reforming step.

A theoretic calculation of the overall catalytic activity in naphthalene reforming at 800 and 850 °C in this combined two reforming step arrangement would lead to an activity of 96.8 and 99.8%, respectively, if using the corresponding experimentally measured conversion values of GS-Al-0.7MgAl-77Ni and CFO-Al-6.2MgAl-59Ni at a superficial velocity of 2 and 2.5 cm/s in Fig. 6, respectively for the first and second reforming step (Fig. 8). For this, for the second reforming step, in a first approximation the same naphthalene conversions measured at 800 and 850 °C were assumed also for naphthalene inlet contents of <2 g and for a superficial velocity of 2 cm/s.

The lower experimentally determined conversion values of 82% and 98.7% compared to the above mentioned calculated values at 800 or 850 °C, respectively, can be explained by the lower naphthalene inlet contents for the second reforming step. This would lead to lower conversions of the catalytic ceramic foam due to a lower saturation of the active sites in competition with H_2S poisoning the Ni sites [9].

It is noteworthy, that the deviation from the experimental to the calculated value is with 1.1 absolute percentage relatively low at 850 °C, whereas at 800 °C a deviation of 14.8 absolute percentage was found. Therefore, at 850 °C, precalculation of the overall catalytic activity of the two-step system is possible by taking a correction factor of 0.989 into account.

Furthermore, the catalytic activity of the catalytic ceramic foam at a superficial velocity of 4.67 cm/s can be calculated to 93.9% from the measured activity of 98.7% at a superficial velocity of 2.5 cm/s and of 93% at a superficial velocity of 5 cm/s (Fig. 8). In this calculation a linear dependence of the activity on the superficial velocity is assumed.

Consequently, if in the first catalytic filter candle step 86.9% naphthalene conversion is realized at a superficial velocity of 2 cm/s and in the second catalytic ceramic foam step 93.9% calculated conversion is realized at a superficial velocity of 4.67 cm/s, an overall naphthalene conversion of 98.1% can be precalculated for the catalytic filter candle with integrated catalytic ceramic foam by taking the correction factor into account (Fig. 8).

This high overall naphthalene conversion at 850 °C in the presence of 100 ppmv H_2S shows that efficient tar reforming using this new type of catalytic filter candle of catalytic layer design is technically feasible. Long-term stability of this type of catalyst under the conditions used in testing in this paper has been demonstrated before [21]. However, real gas validation of this new catalytic candle type, that has already been started [22], over longer test intervals are to be performed in future work to evaluate its applicability on industrial scale.

4. Conclusions

A catalytic 45 ppi ceramic foam and ceramic fiber prepared by using the same impregnation media for catalyst integration have shown comparably high naphthalene conversions of 90% at 800 °C in the presence of H_2S at a superficial velocity of 5 cm/s. Because of the higher rigidity, the 45 ppi catalytic ceramic foam presents the more suitable system for integration in a catalytic filter candle. As result of a catalytic layer screening on SiC ceramic foams, an MgO- Al_2O_3 supported Ni catalyst system with a more than two-fold higher NiO density compared to a SiC catalytic filter candle was identified to show at 800 °C nearly complete naphthalene conversion in the presence of H_2S at a face velocity of 2.5 cm/s. At the target temperature of 850 °C and at a higher superficial velocity of 5 cm/s simulating the conditions for an integrated ceramic foam in a catalytic filter candle, the conversion still achieves 93% with an Al_2O_3 based ceramic foam. Transfer of the most active catalytic layer screened on a SiC based filter candle to an Al_2O_3 based candle has led to a naphthalene conversion of 87%. The overall activity of an Al_2O_3 based catalytic filter candle with an integrated catalytic ceramic foam was precalculated to 98% naphthalene conversion that was by 18% higher than the achieved conversion of a SiC candle so far without integrated catalytic ceramic foam. This indicates the importance of the additional use of a catalytic ceramic foam to provide a technically feasible solution at 850 °C for efficient tar reforming in hot gas cleaning of biomass derived syngas.

Acknowledgments

The authors are grateful to Mrs. Jana Bullinger for the support in the preparation and characterization of the samples.

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